(19) World Intellectual Property Organization International Bureau



(DEGLE COLUMN COLUMN CARDO COLUMN COLUMN COLUMN COLUMN CARDO COLUMN CARDO COLUMN CARDO COLUMN CARDO COLUMN CO

(43) International Publication Date 27 December 2001 (27.12.2001)

PCT

(10) International Publication Number WO 01/98630 A1

(51) International Patent Classification⁷: E21B 43/38, 49/08, 49/10, G01N 30/88

(21) International Application Number: PCT/GB01/02546

(22) International Filing Date: 11 June 2001 (11.06.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data: 0015052.4

21 June 2000 (21.06.2000) GB

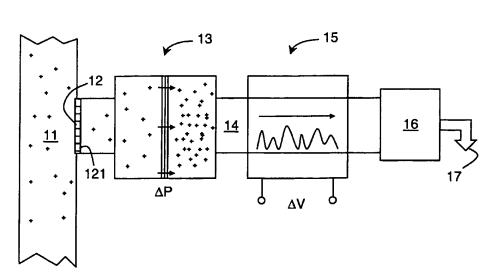
(71) Applicants (for all designated States except US): SCHLUMBERGER TECHNOLOGY B.V. [NL/NL]; Parkstraat 83-89, NL-2514 JG The Hague (NL). PE-TROLEUM RESEARCH AND DEVELOPMENT N.V. [NL/NL]; De Ruyterkade 62, Willemstad, Curacao (AN). SCHLUMBERGER CANADA LIMITED [CA/CA]; 525 - 3rd Avenue S.W., Calgary, Alberta T2P 0G4 (CA). SCHLUMBERGER HOLDINGS LIMITED [-/-]; P.O. Box 71, Craigmuir Chambers, Road Town, Tortola (VG). SCHLUMBERGER LO-GELCO INC. [PA/PA]; 8 Calle Aquilino de la Guardia, Panama City (PA). SCHLUMBERGER OILFIELD ASSISTANCE LIMITED [--/--]; Craigmuir Chambers, Road Town, Tortola (VG). SCHLUMBERGER OVER-SEAS S.A. [PA/PA]; 8 Calle Aquilino de la Guardia, Panama City (PA). SERVICIOS DE PERFILAJES ELECTRONICOS, S.A. [--/--]; Craigmuir Chambers, Road Town, P.O. Box 71, Tortola (VG). SCHLUM-BERGER SEACO INC. [PA/PA]; 8 Calle Aquilino de la Guardia, Panama City (PA). SCHLUMBERGER SER-VICES LIMITED [-/--]; P.O. Box 438, Tortola (VG). SCHLUMBERGER SURENCO S.A. [PA/PA]; 8 Calle Aquilino de la Guardia, Panama City (PA). SERVICES PETROLIERS SCHLUMBERGER [FR/FR]; 42, rue Saint-Dominique, F-75007 Paris (FR).

- (72) Inventors; and
- (75) Inventors/Applicants (for US only): JONES, Timothy, Gareth, John [GB/GB]; 16 Denmark Road, Cottenham, Cambridgeshire CB4 8QS (GB). JIANG, Li [CN/GB]; 47 Almoners Avenue, Cambridge CB1 8NZ (GB). MANZ,

[Continued on next page]

(54) Title: CHEMICAL SENSOR FOR WELLBORE APPLICATIONS

10



(57) Abstract: There is described an analyzing device having two separation units to separate molecular species to detect molecular species in wellbore fluids with both separation units operating under forced flow conditions to provide for an active separation of subterranean wellbore effluent into its components for subsequent analysis.

BEST AVAILABLE COPY

01/08630 A1



Andreas [CH/GB]; 14 The Wilderness, East Molesey, Surrey KT8 0JT (GB). TANTRA, Ratna [ID/GB]; 13 Hendon Park Mansions, Queens Road, Hendon, London NW4 2TG (GB).

- (74) Agent: MACQUET, Christophe; Schlumberger Cambridge Research Limited, Intellectual Property Law Dept., High Cross, Madingley Road, Cambridge CB3 0EL (GB).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,

- MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

- 1 -

Chemical Sensor for Wellbore Applications

The invention relates to a chemical sensor tool for use in downhole analyzing of fluids produced from subterranean formations.

BACKGROUND OF THE INVENTION

Analyzing samples representative of downhole fluids is an 10 important aspect of determining the quality and economic value of a hydrocarbon or water producing formation.

Present day operations obtain an analysis of downhole fluids usually through wireline logging using a formation tester such as the MDT^{mx} tool of Schlumberger Oilfield Services. However, more recently, it was suggested to analyze downhole fluids either through sensors permanently or quasi-permanently installed in a wellbore or through sensor systems mounted on a drillstring. The latter method, if successful implemented, has the advantage of obtaining data while drilling, whereas the former installation could be part of a control system for wellbores and hydrocarbon production, therefrom.

To obtain first estimates of the composition of downhole fluids,

25 the current MDT^{mm} tool uses an optical probe to estimate the
amount of hydrocarbons in the samples collected from the
formation. Other known sensors use resistivity measurements to
discern various components of the formations fluid.

30 To meet demand for chemical measurements of increasing accuracy, it may appear obvious to adapt chemical analysis tools known from chemical laboratory practice to the hostile environment of a subterranean borehole. Such known analysis tools include for example the various types of chromatography, electrochemical and spectral analysis. However, a closer look at the environmental

- 2 -

conditions within a subterranean wellbore lets those attempts appear as futile.

Various types of downhole measurement tools are known. Examples of such tools are found in the United States Patents Nos. 6,023,340; 5,517,024; and 5,351,532 or in the International Patent Application WO 99/00575.

It is therefore an object of the present invention to provide 10 apparatus and methods that would allow the use of chemical analysis tools known per se in a subterranean wellbore.

SUMMARY OF THE INVENTION

15 It was found that many problems associated with the use of sensitive chemical analysis tools are grounded on a lack of purity of samples as acquired from downhole formation.

Therefore, there is provided a wellbore fluid sampling device 20 comprising at least two separation stages for a sample of downhole fluids characterized in that within each of said at least two separation stages components of the sample are separated by an active force.

25 Active forces as contemplated by the present invention may be pressure gradients as generated by pumps, or electrical fields generated by electrodes connected to different potentials, or a combination of both. Each stage may be equipped with its own force generator.

30

A separation stage is defined herein as a device or system that separates fluid phases or, within a fluid phases, molecules or ions according to their chemical or physical properties. Not included in the definition of a separation stage are mesh type filters. Those filters are widely used to remove solid particles from the fluid samples. In contract the separation stages within

- 3 -

the context of the present invention generally assume that the fluid sample at its input have been already subjected to a solid removal process.

- 5 A separation stage in accordance may comprise selective membranes, or chromatographic channels, i.e. paths along which different species migrate with different velocities.
- The molecular target species preferable considered by the present invention are cations such as Ca^{2+} , Mg^{2+} , Sr^{2+} , Ba^{2+} , Na^{+} or K^{+} , anions such as CO_{3}^{2-} , SO_{4}^{2-} , PO_{4}^{3-} or Cl^{-} , various hydrocarbons as encountered in subterranean formations, or gases such as $H_{2}S$, CO_{2} , CH_{4} , or He.
- 15 In a preferred embodiment of the invention, at least one separation unit comprises an ion-selective membrane, or, even more preferable, a potentiometric sensor with an ion-selective membrane.
- 20 The device is preferably adapted to operate as sensor for various downhole applications, including wellbore logging, measurement-while-drilling (MWD), or permanent monitoring, i.e. as a fixed installation within the borehole.
- 25 Another industrial application of the present invention is the management and control of subterranean water reservoirs and aquifers.
- These and other features of the invention, preferred embodiments and variants thereof, possible applications and advantages will become appreciated and understood by those skilled in the art from the following detailed description and drawings.

- 4 -

DRAWINGS

FIG. 1 shows a schematic diagram of the main elements in accordance with the present invention;

5

- FIGs. 2A,B show details of two examples in accordance with the present invention;
- FIG. 3A shows details of a potentiometric sensor with an ionselective membrane as separator as employed in the
 example of FIG 2B;
 - FIG. 3B shows the sensor of FIG. 3A with an additional electrophoretic separation channel;

15

- FIG. 4 illustrates the use of the analyzing tool as wireline logging tool;
- FIG. 5 illustrates the use of the analyzing tool as part of an MWD (measurement-while-drilling) tool;
 - FIG. 6 illustrates the use of the analyzing tool as part of a permanently installed flow monitoring unit in a wellbore; and

25

FIG. 7 illustrates a further variant of an analyzing tool as part of a permanently installed flow monitoring unit in a wellbore.

30

MODE(S) FOR CARRYING OUT THE INVENTION

In FIG. 1, there is schematically illustrated how elements of an analyzing tool in accordance with the present invention interact

- 5 -

to achieve a better separation of the components of a downhole fluid and, hence, more accurate testing results.

According to FIG.1, a flow conduit 11 is provided with an

5 opening 12 through which at least a part of a fluid flowing
through the conduit can enter into a first separation unit 13.

At the outlet of the first separation unit a conduit or flow
channel 14 then provides a flow path to the second separation
unit 15. The outlet of the second separation unit has

10 communicates with a sensor unit 16 used to perform the detection
of the separated species of the flow. An outlet 17 is provided
for the disposal of the fluid that migrated through the device.

The flow conduit 11 may be communicating directly with the

fluids produced from the well. Or, alternatively, the conduit
can be a by-pass of a main conduit carrying at least parts of
the produced fluids. The conduit 11 may contain the original
fluid flow as produced from the formation or a pre-processed
fluid.

20

Between the conduit and the separation units there is a shown a mesh 121 to prevent solid particles from entering the tool.

In the example depicted in FIG 1, the separation units are drawn schematically as membrane type (separation unit 13) and as separation column type (separation unit 15), respectively. The selection of the precise separation mechanism is much a matter of choice and depends on the species involved and upon design considerations. The two separation mechanisms considered for this example are firstly phase selective membranes such as gas stripping membranes (surface selective flow membranes) for gaseous phases and ZrSO₄, PTFE or silicon rubber membranes to separate gas from an aqueous or organic phase. The second mechanism is based on the variation of the migration or

- 6 -

diffusion pattern of a species though a medium, and is usually known as chromatography.

Both units 13, 15 have an independent source of energy providing
5 energy to transport at least part of the fluid through the
separation unit. Sources are conveniently force gradients, such
as pressure gradients, temperature gradients, electrical or
chemical potential gradients. Those gradients can be provided by
pumps, particularly micropumps, electrical generators, heat
10 reservoirs etc.

The detector unit 16 is either a single detector or an array of detectors, either of the same type or a combination of different detectors. Suitable detectors are based on the emission or

15 absorption of electromagnetic waves (UV-Vis, IR, Flourescence, Raman, NMR) or acoustic waves, or on electrochemical reactions (conductivity/resistance, potentiometric, amperometric) or other conventional detectors as used for example in the field of chromatography (FID, ECD). The detector itself is coupled to a control and data acquisition system (not shown), which could be installed either locally, i.e., in vicinity of the sensor, or remotely, e.g. at the surface.

A more detailed illustration of the example is shown in FIG. 2.

25

FIG. 2A shows a chemical sensor and attached sampling interface for a multiphase, multicomponent fluid stream. The flow stream is sampled using the sampling interface, which consists of a pre-filter 121 to remove particulate matter, a pump 131 and a chamber 132 to average the composition of the fluid stream over the time between analyses. The fluid from the sample stream is drawn into the sampling chamber through valve V1 using a pump 131. The pump 131 can be used to mix the fluid by pumping it forwards and backwards in the sample chamber 132. The pump is also able to empty the chamber of the sample by pumping to waste

- 7 -

or replacing the sample fluid with a second fluid from a reservoir, e.g., for the purposes of calibrating the chemical sensor or cleaning the chamber and associated pipe work. The two inlet ports to the sample chamber are controlled by the use of valves V1 and V2.

When a suitable sample has been captured and mixed in the sample chamber 132 valve V2 is closed and the three-way valve V4 is set to pump the fluid sample to waste. The fluid sample is passed through a membrane filter 133 designed to let pass through a pre-determined phase of the fluid.

The separated phase is pumped to the chemical analysis system using the sampling/mixing pump 131 while the extracted component is pumped to the analytical system using a second pump 134 and a suitable solvent for the extracted phase. For example, in the case of extracted carbon dioxide, the solvent could be a dilute solution of sodium hydroxide; the carbon dioxide is solubilised in the alkaline solution and converted to carbonate (or bicarbonate) ions. The flow rate of solvent is controlled by the second pump 134 and is selected to with knowledge of the known rate of diffusion of the component across the separation membrane 133.

When the sample or component for analysis has been pumped to valve **V4** it is switched from waste to the analysis system and an accurately known volume is delivered to the flow line **14** of the analysis system. The volume dose can be controlled either by the delivery pump **134** or using a suitable sample injection system.

30

The injected sample is pumped through the separation system 15, such as a chromatography column or electrophoresis capillary column 151, and the separated components analyzed by a suitable detector, e.g., electrochemical (potentiometric, amperometric) or optical (spectrophotometric or fluorescent) detectors. Valve

- 8 -

V5 can be used to divert certain separated components from the detector to avoid problems of contamination or detector overload.

- 5 In the device shown in FIG. 2B, the separator and detector units are merged into one micro-measurement system as is described in more detail below. The separator unit 15 comprises a ion-selective membrane.
- 10 Ion-selective membrane electrodes are electrochemical electrodes that can be used in the direct measurement of the activity, and hence concentration, of analyte ions in sample solutions, particularly complex organic solutions. Selectivity for one species over another is determined by the nature and chemical composition of the ion-selective membrane and the associated reaction layers used to fabricate the electrode. Such ion-selective membranes serve as an additional component of a classic two-electrode galvanic cell, with the potential developed at the interface between the membrane and the sample solution being directly or indirectly related to the activity of the analyte ions in the sample solution.

The measurement principle of electrochemical cells incorporating ion-selective membrane electrodes is quite simple. Two

25 electrodes are separated by an ion-selective membrane, with the solution on one side of the membrane being an internal reference solution of known composition and including ions to which one electrode, referred to as the internal electrode, and the membrane respond, and the solution on the other side of the

30 membrane being a sample solution in contact with the other electrode, referred to as the external reference electrode.

In such electrochemical cells the phase-boundary potentials will be constant except for the membrane potential which is the 35 difference in the electrical potential between the internal WO 01/98630

- 9 -

PCT/GB01/02546

reference solution and the sample solution; the variation in this membrane potential being an indication of the activity of the analyte ions in the sample solution. In practice, the internal electrode, the internal reference solution and the ionselective membrane are often housed in a single unit to provide an ion-selective electrode. In this arrangement the voltage is measured as an electromotive force (EMF) between the ionselective electrode (ISE) and the reference electrode (RE) according to the formula EMF = E_{ISE} - E_{RE} .

10

The measurement system can be a microfabricated potentiometric sensor as disclosed for example in a paper by Uhlig et al entitled "Miniaturized Ion-Selective Chip Electrode for Sensor Application" as published in Analytical Chemistry, Vol. 69, No.

15 19, pages 4032 to 4038. These miniaturized sensors are fabricated by depositing a polymeric ion-selective membrane into anisotropically etched wells in a silicon wafer, and, in use, a sample solution is brought into contact with one side of the silicon wafer.

20

An improved and more rugged version of such a system which includes a separation stage and detection on one chip is described in FIG. 3.

25 In FIG. 3 there is shown the sensor **31** as fabricated in a substrate chip **32**.

The chip 32 includes flow channel 33, in this embodiment of linear section, which includes an inlet port 35 and an outlet 30 port 37 through which a sample solution is in use fed. In this embodiment the flow channel 33 is 10 mm in length, 200 μ m in width and 20 μ m in depth.

The chip 32 further includes a chamber 39 with an ion-selective 35 membrane 311. The chamber 39 comprises a first, main region

- 10 -

313, in this embodiment of flattened U-shaped section, which includes first and second ports 315, 317 and a second, narrow junction region 319 that communicates directly with the flow channel 33 and extends substantially between midpoints of the 5 main region 313 and the flow channel 33. In this embodiment, the main region 13 is 12 mm in length, 200 μ m in width and 20 μ m in depth, the first and second ports 315, 317 are 800 μ m in diameter, and the junction region 319 is 830 μ m in length, 20 μ m in width and 20 μ m in depth.

10

In this embodiment the chamber 39 is completely filled with ion-selective membrane 311 as shown. In other embodiments only the junction region 319 of the chamber 39 can be filled with the ion-selective membrane 311 or the U-shaped main region 313 of the chamber 39.

In another embodiment the chamber 39 can include an inert, porous supporting material, such as a ceramic, which is provided to support the ion-selective membrane 311 and improve the 20 mechanical stability thereof.

The chip 32 is fabricated from two plates, in this embodiment composed of microsheet glass. In an alternative embodiment the plates could be formed of silicon wafers. In a first step, one of the plates is etched by HF wet etching to form wells which define the flow channel 33 and the main and junction regions 313, 319 of the chamber 39, with the wells having the respective dimensions mentioned hereinabove. In a second step, four holes are drilled, in this embodiment by ultrasonic abrasion, into the other plate so as to provide the inlet and outlet ports 35, 37 of the flow channel 33 and the first and second ports 315, 317 of the chamber 39. In a third step, the two plates are bonded together by direct fusion bonding. In a fourth step, the junction region 319 of chamber 39 is filled with an organic

- 11 -

cocktail that provides the ion-selective membrane 311. Filling is achieved by maintaining a gas flow, typically of an inert gas such as argon, through the flow channel 33 and introducing a predetermined volume of the organic cocktail into one of the ports 315, 317 of the chamber 39. In this way, the main and junction regions 313, 319 of the chamber 39 are filled with the organic cocktail; organic cocktail being prevented from entering the flow channel 33 by the gas flow maintained therethrough. Where the chamber 39 is to include an inert, porous supporting material, this material is introduced prior to or after fusing together the two plates. In a fifth and final step, the chip 32 is allowed to stand until the solvent in the organic cocktail of the ion-selective membrane 311 has evaporated and a dry ion-selective membrane 311 is formed. Typically, the chip 32 is dried in a desiccator.

In this embodiment the organic cocktail comprises
tetrahydrofuran (THF) as a solvent, o-nitrophenyloctyl ether (oNOPE) as a solvent mediator, polyvinyl chloride (PVC) as a

20 polymeric matrix material, potassium tetrakis(4chlorophenyl)borate (TPB) as a lipophilic salt for reducing
electrical resistance, and an ion-transfer agent. Other
suitable polymeric matrix materials include fluorosilicone
elastomers that have a relatively low resistance and high

25 dielectric constant.

In a preferred embodiment the chamber 39 can be surface treated so as to be of increased hydrophobicity. Preferably, the chamber 39 is silanized by treating with a silane solution.

30 Appropriate silane solutions include the siloxane based solution Repelcote™ and 5 % dimethylchlorosilane in carbon tetrachloride. In practice, the chamber 39 is treated after bonding together the two plates by feeding a metered volume of silane solution, typically using a syringe needle, into one of the ports 315, 317 of the chamber 39 and simultaneously applying a vacuum,

- 12 -

typically using a vacuum pump, to the other of the ports 315, 317 of the chamber 39 so as to fill the same. In order to prevent the silane solution entering the flow channel 33, a gas flow, typically an inert gas such as argon, is maintained in the flow channel 33. The silane solution is maintained in the chamber 39 for a short time, typically from 2 to 3 minutes, and then completely withdrawn using the vacuum pump. This process is then repeated so as to ensure complete silanization of the chamber 39.

10

The sensor 31 further comprises a first tubular section 321, one of the ends of which is enlarged and bonded to the chip 32, in this embodiment by an epoxy resin, so as to overlie the first port 315 of the chamber 39; the first tubular section 321 defining a reservoir which contains an internal reference solution, in this embodiment 0.1 M of KCl.

The sensor 1 further comprises an electrode element 325, in this embodiment an Ag/AgCl wire, disposed in the reference solution 20 contained by the first tubular section 321.

The sensor 31 further comprises a second tubular section 327, one of the ends of which is enlarged and bonded to the chip 32, in this embodiment by an epoxy resin, so as to overlie the outlet port 37 of the flow channel 33; the second tubular section 327 defining a reservoir for containing the sample solution fed through the flow channel 33.

The sensor 1 further comprises a reference electrode 329

30 disposed in the second tubular section 327 so as to contact the sample solution when contained therein. In this embodiment the reference electrode 329 comprises a FlexrefTM minaturized Ag/AgCl electrode as available from World Precision Instruments of Stevenage, UK.

- 13 -

The sensor 1 further comprises a third tubular section 331, in this embodiment a fused silica capillary tube, bonded to the chip 32, in this embodiment by an epoxy resin, so as to overlie the inlet port 35 of the flow channel 33.

With this configuration, the ion-selective membrane 311, the reference solution and the electrode element 325 together define an ion-selective electrode, such that, on feeding a sample solution through the flow channel 33, a potential is developed across the ion-selective electrode and the reference electrode 329 corresponding to the membrane potential which is the electrical potential between the reference solution and the sample solution and is representative of the activity of the analyte ions in the sample solution.

The measurement system further comprises a solution feeder 14, which connects to the first separation unit as shown in FIG 2B. The measurement system further comprises a data acquisition unit 349 for logging the electromotive force developed across the ion-selective electrode and the reference electrode 329 of the sensor 31. In this embodiment the data acquisition unit 349 comprises a PICO-LOGTM data acquisition system as available from Pico-Technology of Cambridge, UK connected to the ion-selective electrode and the reference electrode 329 through a buffer amplifier for converting the high impedance voltage to a low impedance voltage.

In use, the solution feeder 14 configured to feed a sample solution at a predetermined flow rate through the flow channel 33 of the sensor 31. As this sample solution is fed through the flow channel 33 the electromotive force generated across the ion-selective electrode and the reference electrode 329 is logged by the data acquisition unit 349, which data can be used

WO 01/98630

- 14 -

PCT/GB01/02546

to provide an on-line measurement of the activity of the analyte ions in the sample solution.

The system further comprises a pump 345 connected by tubing 347 to the sample solution reservoir defined by the second tubular section 327 for feeding the measured solution to waste.

The example of FIG. 3A can be combined with a further separation method, preferably mounted onto the same substrate.

10

In FIG. 3B such a further separation stage is shown added to the ion selective sensor of FIG. 3A. Essentially, the separation stage comprises a capillary electrophoretic channel. With an appropriate voltage applied to the buffer fluid reservoirs 362, 15 363, a sample migrates through the basic electrophoretic channel 361. To load samples into the electrophoretic channel 361, the system operates a cross-flow mechanism. As in the previous example, the initial sample flow is fed via feeder 14 and tube 331 to the inlet port 35. From the inlet port the sample flow is 20 quided through channel 351 to a waste outlet 352. By reducing the voltage across inlet 35 and outlet 352 below the voltage applied to the buffer fluid reservoirs 362, 363, a sample "plug" located at the crossing between the two channels 351, 361 flows along the capillary electrophoretic separation channel 361. In 25 the electrophoretic separation channel 361, the sample is separated according the mobility of its components. Near the end of channel 361, an ion-selective sensor 31 (as described in the previous example) provides an additional separation combined with a quantitative measurement of the ionic concentration in 30 the sample. Fractions of the passing sample are absorbed by the ion-selective membrane and cause a change in the potential difference between electrodes 327 and 325. The system control

and data acquisition unit 349 monitors the change.

- 15 -

WO 01/98630 PCT/GB01/02546

In the following, a tool in accordance with the present invention is depicted in various types of downhole measurements.

In FIG. 4, there is shown a formation testing apparatus 410 held 5 on a wireline 412 within a wellbore 414. The apparatus 410 is a well- known modular dynamic tester (MDT, Mark of Schlumberger) as described in the co-owned U.S. Pat. No. 3,859,851 to Urbanosky U.S. Pat. No. 3,780,575 to Urbanosky and Pat. No. 4,994,671 to Safinya et al., with this known tester being 10 modified by introduction of an analyzing tool 416 as described in detail above. The modular dynamics tester comprises body 420 approximately 30m long and containing a main flowline bus or conduit 422. The analysing tool 416 communicates with the flowline 422 via opening 417. In addition to the novel sensor 15 system 416, the testing apparatus comprises an optical fluid analyser 430 within the lower part of the flowline 422. The flow through the flowline 422 is driven by means of a pump 432 located towards the upper end of the flowline 422. Hydraulic arms 434 and counterarms 435 are attached external to the body 20 420 and carry a sample probe tip 436 for sampling fluid. The base of the probing tip 436 is isolated from the wellbore 414 by an o-ring 440, or other sealing devices (packers).

Before completion of a well, the modular dynamics tester is

lowered into the well on the wireline 412. After reaching a
target depth, i.e., the layer of the formation which is to be
sampled (here: 442), the hydraulic arms 434 are extended to
engage the sample probe tip 436 with the formation. The o-ring
440 at the base of the sample probe 436 forms a seal between the
side of the wellbore 444 and the formation 442 into which the
probe 436 is inserted and prevents the sample probe 436 from
acquiring fluid directly from the borehole 414.

Once the sample probe 436 is inserted into the formation 442, an

electrical signal is passed down the wireline 412 from the surface so as to start the pump 432 and the sensor systems 416 and 430 to begin sampling of a sample of fluid from the formation 442. The first separation unit of the analyzing system 5 416 is provided with a silicon rubber membrane. The following electrokinetic separation in the ion-selective channel and the potentiometric detector are adapted to measure the metal ion (Me²⁺⁾ content of the formation effluent.

- 10 A further possible application of the novel sensor and separation system is in the field of measurement-while-drilling (MWD). The principle of MWD measurements is known and disclosed in a vast amount of literature, including for example United States Patent No. 5,445,228, entitled "Method and apparatus for formation sampling during the drilling of a hydrocarbon well".
- In FIG. 5, there is shown a wellbore **511** and the lower part of a drill string **512** including the bottom-hole-assembly (BHA) **510**. The BHA carries at its apex the drill bit **513**. It includes further drill collars that are used to mount additional
 - equipment such as a telemetry sub **514** and a sensor sub **515**. The telemetry sub provides a telemetry link to the surface, for example via mud-pulse telemetry. The sensor sub includes the novel analyzing unit **516** as described above. The analyzing unit
- 25 **516** collects fluids from the wellbore via a small recess **517** protected from debris and other particles by a metal mesh.

During drilling operation wellbore fluid enters the recess 517 and, hence, the first separation unit of the analyzing tool 516.

30 After further separation and detection as described above (FIGs. 2 and 3), the results are transmitted from the data acquisition unit to the telemetry unit 514, converted into telemetry signals and transmitted to the surface.

35 A third application is illustrated in FIG. 6. It shows a

- 17 -

venturi-type flowmeter 610, as well known in the industry and described for example in the United States Patent No. 5,736,650. Mounted on production tubing or casing 612, the flowmeter is installed at a location within the well 611 with a wired connection 613 to the surface following known procedures as disclosed for example in the United States Patent No. 5,829,520.

The flowmeter consists essentially of a constriction or throat 614 and two pressure taps 618, 619 located conventionally at the entrance and the position of maximum constriction, respectively. Usually the venturi is combined with a densionmeter 615 located further up- or downstream.

The novel analyzing unit **616** is preferably located downstream

15 from the venturi to take advantage of the mixing effect the

venturi has on the flow. A recess **617** protected by a metal mesh

provides an inlet to the unit.

During production wellbore fluid enters the recess 617 and,
20 hence, the first separation unit of the analyzing tool 616.

After further separation and detection as described above (FIGs. 2 and 3), the results are transmitted from the data acquisition unit to the surface via the wires 613.

25 A further example of the present invention is shown in FIG. 7.

The illustrated device is part of a downhole installation 710
employed to monitor the flow through a downhole conduit 712. The
device by-passes a flow restriction a The monitoring system
comprises three pressure sensors 721,722,723 and six valves 73130 736 located at various position along a conduit 74. The conduit
has a first opening 741 covered by a mesh 751. The mesh 751
protects a subsequent phase filter 752. Also positioned along
the conduit 74 are a conductivity detector 76 and a mixing
chamber 77 followed by a pumping system 78. The pumping system
35 78 is operated through thermal expansion. The necessary thermal
energy is provided by an electrical heating coil 781. The output

flowline leads to the on-chip separation and analyzing unit

- 18 -

described in FIG. 3.

In operation a multiphase flow 711 is produced from the well and pumped through the conduit 712. A sample from the main conduit 5 is collected through the phase filter 752 (a water saturated ceramic with pore sizes below 1 micron) that allows only the aqueous phase to pass. The fluid sample passes through the filter under a pressure gradient temporarily generated by closing the flow restricting system 713. The pressure gradient 10 can be measured using the pressure transducers 721, 722. When the valve 731 is opened the water sample passes through a conductivity detector 76. The conductivity detector is employed to determine the salinity of the water. Valve 732 is used to release unwanted samples. For further treatment, the sample is 15 collected in the mixing chamber 77 where one or more samples can be mixed to give an averaged representative sample of the fluid over a collection interval. A small pumping system, e.g. a thermal expansion pump, is used to feed a controlled flow into the sensor system for quantitative analysis as described above 20 (FIG. 3). The flow is controlled using valve 736 and the pressure sensor 723. In preparation for further sampling, the conduit 74 can be flushed via valve 735.

The above examples illustrate possible uses of the novel
25 analyzing tool, but are not meant to exclude other possible
application of the analyzing tool in the field of wellbore fluid
analysis.

- 19 -

CLAIMS

- A wellbore effluent analyzing device comprising a main conduit carrying in operation said wellbore effluent, 5 a sample channel communicating through at least one opening with said main conduit, a first separation stage generating a forced flow of said effluent through a first separation member thereby separating from said effluent a fluid sample according to 10 chemical or physical properties; a second separation stage generating a forced flow of said sample through a second separation member thereby further separating said sample according to chemical or physical properties; and 15 a sensor unit to detect components of said further separated sample.
- An analyzing device according to claim 1 wherein at least one of the separation stages is adapted to separate
 hydrocarbon and aqueous phases in the effluent.
 - 3. An analyzing device according to claim 1 wherein at least one of the separation stages comprises a migration path or column filled with material providing different migration velocities to different molecules.
 - 4. An analyzing device according to claim 1 wherein at least one of the separation stages comprises a membrane as separation member.

5. An analyzing device according to claim 4 wherein the membrane is made of material selected from a group comprising PTFE, ZrSO₄, or silicon rubber.

25

30

35 6. An analyzing device according to claim 4 wherein the

- 20 -

membrane is ion-selective.

- An analyzing device according to claim 1 comprising a
 pumping system generating a forced flow through at least one
 of the separation members.
 - 8. An analyzing device according to claim 1 comprising an electrical voltage generator to generate a forced flow through at least one of the separation members.

10

25

- An analyzing device according to claim 1 wherein at least one of the separation units and the sensor unit are microfabricated.
- 15 10. An analyzing device according to claim 1 wherein at least one of the separation units and the sensor unit are mounted on a common substrate.
- 11. An analyzing device according to claim 1 wherein the sensor unit is sensitive to charged atoms or molecules.
 - 12. An analyzing device according to claim 11 wherein the sensor unit is sensitive to charged atoms or molecules selected from a group consisting of Ca^{2+} , Mg^{2+} , Sr^{2+} , Ba^{2+} , Na^{+} , K^{+} , CO_3^{2-} , SO_4^{2-} , PO_4^{3-} and $C1^{-}$.
 - 13. An analyzing device according to claim 11 wherein the sensor unit comprises a potentiometric sensor.
- 30 14. An analyzing device according to claim 1 wherein the sensor is sensitive to organic molecules.
- 15. An analyzing device according to claim 1 housed in a body adapted to engage with a wireline and to be suspended from said wireline.

- 21 -

- 16. An analyzing device according to claim 1 housed in a body mounted on a drill string.
- 5 17. An analyzing device according to claim 1 housed in a body mounted on a production or casing well tubular.
- 18. An analyzing device according to claim 1 further comprising a solid removal filter or mesh located in flow direction
 10 before said first separation stage.



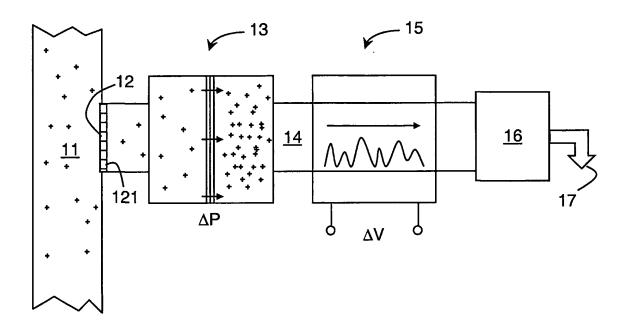


FIG. 1

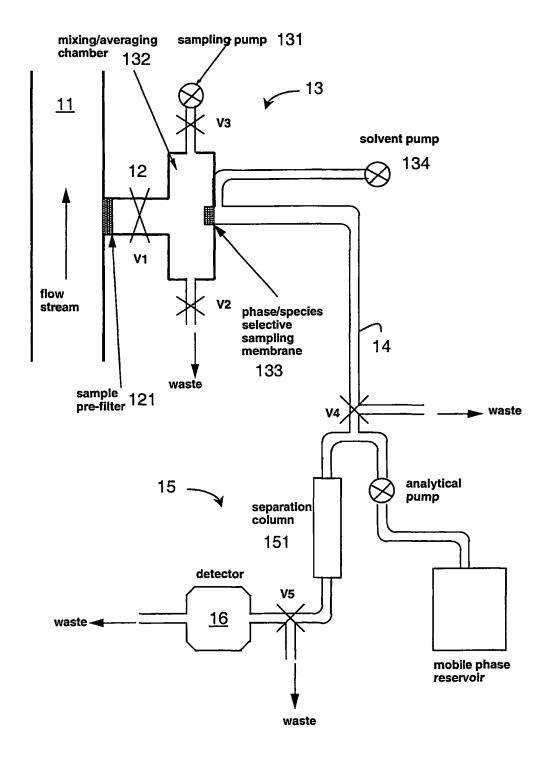


FIG. 2A

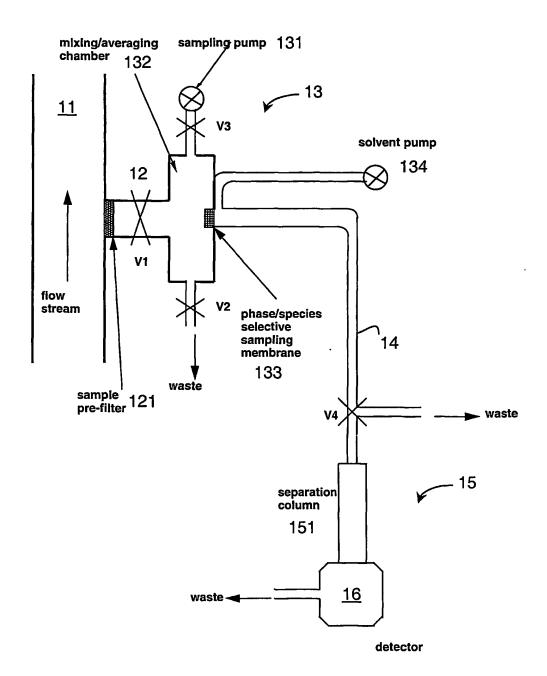


FIG. 2B

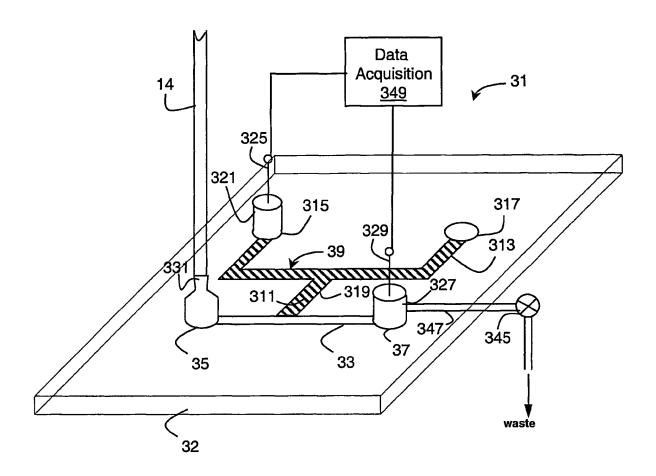


FIG. 3A

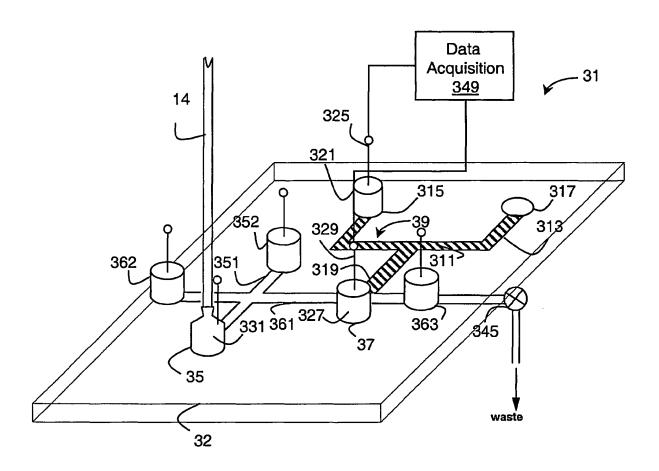
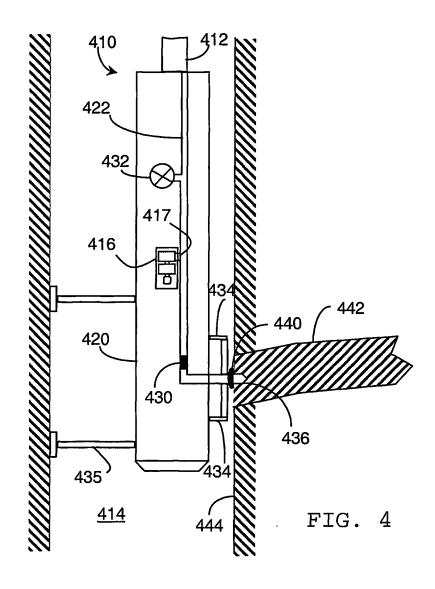
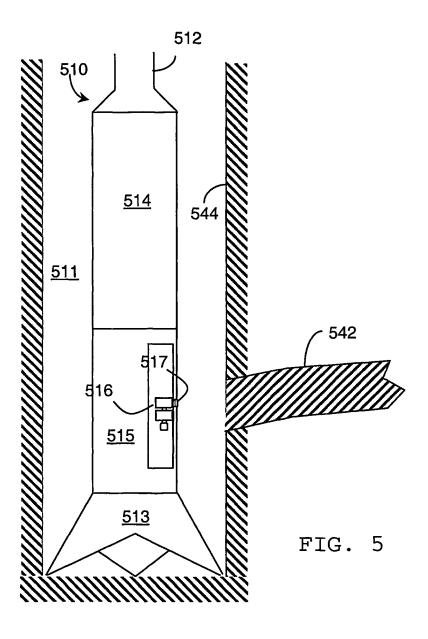
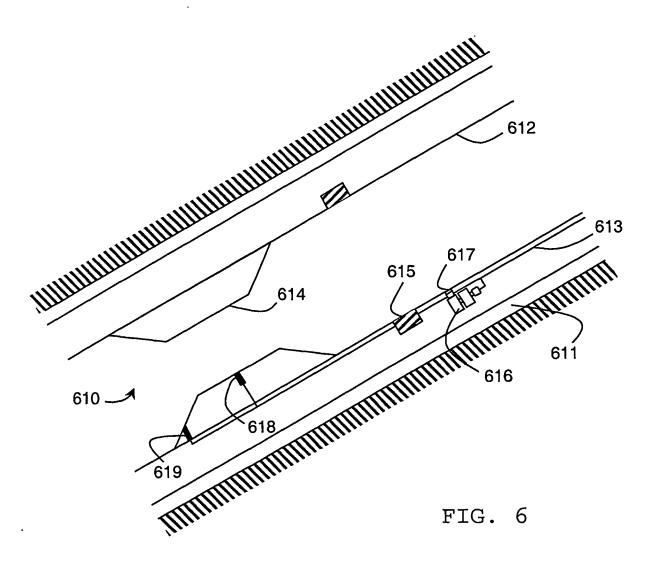


FIG. 3B







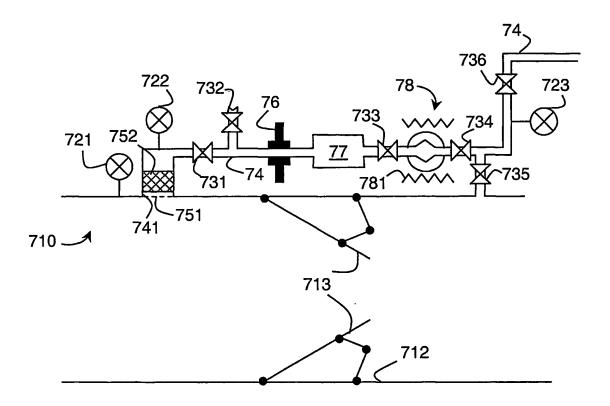


FIG. 7

INTERNATIONAL SEARCH REPORT

in snal Application No PCT/GB 01/02546

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 E21B43/38 E21B49/08 E21B49/10 G01N30/88 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 E21B G01N Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to dalm No. X US 4 739 654 A (PILIKINGTON PAUL; 1-3,7,DISTEFANO MARK; MARVIN ALLEN) 11-18 26 April 1988 (1988-04-26) Y column 3, line 61 -column 6, line 58; 4-6.9.10figures 1,2 X US 4 661 459 A (HIRTZ PAUL N) 1,3,7,8, 28 April 1987 (1987-04-28) 11-14 column 3, line 17 -column 4, line 64; figures 1-3 Υ US 5 147 561 A (BURGE SCOTT R ET AL) 4-6 15 September 1992 (1992-09-15) column 4, line 55 -column 5, line 9; claims 8,24; figures 1-6 -/--Further documents are listed in the continuation of box C. Patent family members are listed in annex. Special categories of cited documents: "I later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance invention "E" earlier document but published on or after the International filing date "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "O" document referring to an oral disclosure, use, exhibition or document published prior to the international filling date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of malling of the international search report 10 September 2001 19/09/2001 Name and mailing address of the ISA Authorized officer European Patent Office, P.B. 5616 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 van Berlo, A

INTERNATIONAL SEARCH REPORT

In nal Application No
PCT/GB 01/02546

| | | PCT/GB 01 | ./ UZ340 |
|-------------|--|-----------------------|----------|
| C.(Continua | ation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. | |
| Y | US 5 673 752 A (SCUDDER PAT ET AL) 7 October 1997 (1997-10-07) column 3, line 10-25; figures 1-4 | | 4-6 |
| Y | 7 October 1997 (1997-10-07) column 3, line 10-25; figures 1-4 US 6 033 546 A (RAMSEY J MICHAEL) 7 March 2000 (2000-03-07) abstract; figures 7,8,12,30 | | 9,10 |
| | | | |
| | | | : |
| | 10 (continuation of second sheet) (July 1892) | | |

INTERNATIONAL SEARCH REPORT

iformation on patent family members

Int onal Application No PCT/GB 01/02546

| Patent document cited in search report | | Publication date | | Patent family member(s) | Publication date |
|---|---|---------------------|--|--|--|
| US 4739654 | A | 26-04-1988 | GB NL | 2216569 A ,B 8800943 A | 11-10-1989 01-11-1989 |
| US 4661459 | A | 28-04-1987 | IT JP NZ PH | 1199346 B 62222140 A 218613 A 22734 A | 30-12-1988 30-09-1987 26-04-1989 28-11-1988 |
| US 5147561 | Α | 15-09-1992 | NONE | | |
| US 5673752 | А | 07-10-1997 | NONE | | |
| US 6033546 | A | 07-03-2000 | US US US AU CA CN EP JP WO | 5858195 A 6001229 A 6010607 A 6010608 A 701348 B2 3150895 A 2196429 A1 1168720 A ,B 0775306 A1 10507516 T 9604547 A1 | 12-01-1999 14-12-1999 04-01-2000 04-01-2000 28-01-1999 04-03-1996 15-02-1996 24-12-1997 28-05-1997 21-07-1998 15-02-1996 |

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

| Defects in the images | include but are not limited to the items checked: |
|-----------------------|---|
| ☐ BLACK BORDERS | |
| ☐ IMAGE CUT OFF A | T TOP. BOTTOM OR SIDES |
| FADED TEXT OR D | PRAWING |
| BLURRED OR ILLE | EGIBLE TEXT OR DRAWING |
| ☐ SKEWED/SLANTEI |) IMAGES |
| COLOR OR BLACK | AND WHITE PHOTOGRAPHS |
| ☐ GRAY SCALE DOC | UMENTS |
| ☐ LÎNES OR MARKS | ON ORIGINAL DOCUMENT |
| ☐ REFERENCE(S) OF | R EXHIBIT(S) SUBMITTED ARE POOR QUALITY |
| OTHER. | |

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.